Shaharyar Ahmed   Reading assignment #7

7.1 Real gases and ideal gases

Ideal gas law accurately describes ~~heat by~~
He but not H_2O

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real gases follow ideal gas law at low density
and high temperature.

7.2 Equations of state for real gases and their
range of applicability.

van der waals : $p = \dfrac{RT}{V_m - b} - \dfrac{a}{V^2_m}$

Redlich-kwong : $p = \dfrac{RT}{V_m - b} - \dfrac{a}{\sqrt{T}} \dfrac{1}{V_m(V_m+b)} = \dfrac{nRT}{V-nb} - \dfrac{n^2a}{\sqrt{T}} \dfrac{1}{V(V+n}$

Both account for $a =$ attractive intermolecular potential

$b =$ minimum value of mole of molecules

Equilibrium pressure is called the vapor pressure of
the liquid.

Critical temperature — temperature at which range of
Vm has shrunk to single values

Pc and Vc — Critical constants.

7.3 The compression factor. $z > 1$ real gas exerts
                                              greater pressure

$z = \dfrac{V_m}{V_{ideal}} = \dfrac{PV_m}{RT}$

Z decreases with pressure at constant T

Z increases with T.

Boyle temperature $T_B = \dfrac{a}{Rb}$

7.4 Law of corresponding states.

Different gases have the same equation of
state if each gas is described by
dimentionless parameters.

$$T_r = \frac{t}{T_c} \qquad P_r = \frac{P}{P_c} \qquad V_{mr} = \frac{V_m}{V_{mc}}$$

Law of corresponding states

$$Z_c = \frac{P_c V_c}{R \cdot T_c} \longrightarrow \text{Independent of } a \text{ and } b$$

7.5 Fugacity and the equilibrium constant for real gases.

$$\mu(T,P) = \mu^\circ(T) + RT \ln \frac{f}{f^\circ} \longleftarrow f = \text{fugacity of gas}$$

$$\ln f = \ln P + \int_0^P \frac{Z-1}{P'} \, dP' \qquad \qquad \downarrow \text{pressure that a gas exerts.}$$

$\gamma = $ fugacity coefficient

8.1 What determines the relative stability of the solid, liquid, and Gas phases.

- most stable in solid at low temp.
- most stable in gas at high temp.

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

$$S_m \, gas > S_m \, liquid > S_m^{\,solid}$$

T_s = sublimation temperature

Triple point = all 3 phases coexist in equilibrium.

8.2 The pressure-temperature phase diagram.

Phase diagram - graphically shows at a given P or T what phase exists.

Coexistence curve - point at which 2 phases exist.

At critical point the densities of liquid and gas are equal.

ΔH sublimation = ΔH fusion + ΔH vaporization.

Phase diagrams are more complex for other substances as more than 1 solid phase may exist.

8.3 The phase rule

Coexistence of 2 phases requires that chemical potential is equal

$$\mu_\alpha(T,P) = \mu_B(T,P) = \mu_\gamma(T,P)$$

pure substance — 2 DOF

Two phase — 1 DOF

3 phase — 0 DOF

Phase rule — Links DOF to # of phases

$$F = 3 - p$$
$\uparrow$
# of phases

8.4 Pressure volume and P-V-T phase diagrams.

A P-V diagram and P-T diagram may be combined to produce a P-V-T diagram.

A P-V-T diagram is has 3 parameters.

8.5 Providing a theoretical basis for the P-T Phase diagram.

Clapeyron equation $\dfrac{dP}{dT} = \dfrac{\Delta S_m}{P V_m}$

$\downarrow$

allows us to calculate slope of the coexistence curve.

Troutons rule — $\Delta S_{vapor} \simeq 80 \dfrac{J}{mol \cdot k}$ for Liquids

Trouton's rule only works for substances without strong interactions

for these ΔS vapor $\geq$ 90 $\frac{J}{mol\cdot k}$

8.6 Using the Clausius-Clapeyron equation to calculate vapor pressure as a function of T.

$\downarrow$

$$\frac{dP}{P} = \frac{\Delta H \text{ vaporization}}{R} \frac{dT}{T^2}$$

Vapor pressure rises exponentially with temperature.

8.7 The vapor pressure of a pure substance depends on the applied pressure

$$RT \ln\left(\frac{P}{p^*}\right) = V_m^{liquid} (P-p^*)$$

Vapor pressure of the substance will be dependent upon applied pressure.

8.8 Surface tension.

under gravity a water droplet will become a sphere bc of attractive forces. because this minimized the surface area

$$dA = \gamma d\sigma$$

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Helmholtz ⟍ surface tension